Calculation of the Second Virial Coefficient of Gases.

By

T. S. Wheeler.

(*Received for publication, 2nd Dec., 1932.*)

In a recent paper [1] the author has shown from thermodynamical and dimensional considerations, that the second virial coefficient (B) of a gas consisting of small spherically symmetrical particles, all of one kind, between each pair of which at a distance r from one another there exist two forces given by λ/r^n (repulsive) and μ/r^m (attractive), should be capable of approximate expression by an equation of the form

$$B = C_1 \,(\lambda/T)^{3/(n-1)} + C_2 \,(\mu/T)^{3/(m-1)} \quad \text{.....................(1)}$$

C_1 and C_2 are constants and T is the absolute temperature. Lennard-Jones, in a series of classical papers [2] has shown that for the type of gas under consideration,

$$B = (2/3)\pi N \Big[(\lambda/(n-1))\ (m-1)/\mu\Big]^{3/(n-m)} F(y) \quad \text{.........(2)}$$

where N is the number of molecules in the quantity of gas to which B refers, and

$$F(y) = y^{3/(n-m)} \Big[\Gamma(n-4)/(n-1) - \sum_{q=1}^{\infty} f(q) y^{q}\Big] \quad \text{...........(3)}$$

[1] Phil. Mag. *13*, 604, 1932.

[2] Proc. Roy. Soc. *112*, 214, 1926.

In this expression,

$$y = [\ \mu/((m-1)\ \mathrm{kT})]\ [((n-1)/\lambda)\mathrm{kT}\ ]^{(m-1)/(n-1)} \quad \text{...........(4)}$$

and the coefficients $f(q)$ are written for,

$$f(q) = 3\left[\Gamma(\ (q\ \overline{m-1}-3)/(n-1)\ )\right] q\,!(n-1) \quad \text{...........(5)}$$

Lennard-Jones determined by a graphical method values of (m, n) to fit (2) and from these calculated the corresponding values of λ and μ.

It has now been found that the second virial coefficients of the gases considered by Lennard-Jones can be expressed by equations of the type of (1), and that the values of (m, n) which are suitable for (2) are also suitable for (1). Table I shows the application of (1) to the calculation of the second virial coefficients of helium, neon, argon, hydrogen and nitrogen using values of (m, n) chosen from the range given by Lennard-Jones. For nitrogen and argon results obtained by taking (m, n) equal to (4, 9·3) are also given. B refers to 1 c.c. of gas at N. T. P.

The equations employed are as follows:—

Helium (5, 11). $\mathrm{B} \times 10^4 = 43{\cdot}5/\mathrm{T}^{3/(11-1)} - 193/\mathrm{T}^{3/(5-1)}$ ....(6)

Neon (5, 9). $\mathrm{B} \times 10^4 = 150/\mathrm{T}^{3/(9-1)} - 922/\mathrm{T}^{3/(5-1)}$ ....(7)

Argon (5, 9) $\mathrm{B} \times 10^4 = 475/\mathrm{T}^{3/(9-1)} - 4600/\mathrm{T}^{3/(5-1)}$ ....(8)

Argon (4, 9·3). $\mathrm{B} \times 10^4 = 251/\mathrm{T}^{3/(9\cdot3-1)} - 11{,}800/\mathrm{T}^{3/(4-1)}$ ......(9)

Hydrogen (5, 9) $\mathrm{B} \times 10^4 = 174/\mathrm{T}^{3/(9-1)} - 1010/\mathrm{T}^{3/(5-1)}$ ......(10)

Nitrogen (5, 9) $\mathrm{B} \times 10^4 = 560/\mathrm{T}^{3/(9-1)} - 5000/\mathrm{T}^{3/(5-1)}$ ......(11)

Nitrogen (4, 9·3) $\mathrm{B} \times 10^4 = 293/\mathrm{T}^{3/(9.3-1)} - 12{,}000/\mathrm{T}^{3/(4-1)}$ ...(12)

It will be seen that the agreement obtained is not unsatisfactory.

TABLE I.

Observed and Calculated Values of B.

Temp.	Helium		Neon		Argon			Hydrogen		Nitrogen		
C°	B′* Obs.	B′ Calc. (6)†	B′ Obs.	B′ Calc. (7)	B′ Obs.	B′ Calc. (8)	B′ Calc. (9)	B′ Obs.	B′ Calc. (10)	B′ Obs.	B′ Calc. (11)	B′ Calc. (12)
−258·0	−6·1	−6·0	...	...	...	...	...	...	...	...	...	...
−208·0	4·2	4·1	...	...	...	...	...	...	...	...	...	...
−183·0	4·7	4·7	...	...	...	...	...	−2·5	−2·5	...	...	...
−182·5	...	...	−3·7	−3·7	...	...	...	...	...	...	...	...
−150·0	...	...	0	0·3	...	...	...	1·3	1·2	...	...	...
−130·0	...	...	...	...	...	...	...	...	...	−35·6	−33·5	−34·5
−100	...	...	2·9	2·5	−28·7	−27·4	−28·9	1·1	4·1	−23·1	−23·4	−23·6
−50	...	...	4·1	3·7	−16·9	−17·2	−17·0	5·4	5·4	−11·8	−13·0	−11·8
0	5·3	5·2	4·8	4·5	−9·9	−10·6	−9·8	6·2	6·2	−4·6	−6·2	−4·9
50	5·2	5·2	...	...	−4·9	−5·9	−5·3	6·8	6·7	−0·1	−1·5	−0·6
100	5·1	5·1	5·3	5·5	−1·9	−2·4	−1·8	6·9	7·0	2·7	2·0	2·8
150	...	...	...	...	0·5	−0·1	0·6	...	...	5·1	4·2	4·9
200	4·9	4·9	5·8	5·8	2·1	2·0	2·5	7·0	7·3	6·8	6·2	6·6
300	4·7	4·7	6·1	5·9	5·0	4·6	5·1	...	...	9·2	9·2	9·1
400	4·6	4·7	6·1	6·0	6·8	6·3	6·6	...	...	10·5	11·1	10·3

* $B' = B \times 10^4$ † These numbers refer to the corresponding equations. The observed values of B are taken from the sources used by Lennard-Jones.

The relations involved between (1) and (2) can be deduced as follows :—

Combining (2), (3) and (4) we have,

$$B=(2/3)\pi N\left[\left\{\lambda/(kT(n-1))\right\}^{3/(n-1)}\Gamma\left((n-4)/(n-1)\right)-\right.$$

$$\left.\left\{\lambda/(kT(n-1))\right\}^{3/(n-1)}\left\{\sum_{q=1}^{\infty} f(q)y^{q}\right\}\right] \ldots \qquad \ldots \quad (13)$$

From (13) it is clear that in order that (1) and (2) should correspond Σ and $y^{3/(m-1)}$ should be related by an equation of the first degree over the range of variation of y. Actually a plot of Σ against $y^{3/(5-1)}$ gives a flat curve which approximates to a straight line.

We put therefore in (13),

$$\sum_{q=1}^{\infty} f(q)y^{q}=k_1 y^{3/(m-1)}-k_2 \qquad \ldots \qquad \ldots \qquad \ldots \quad (14)$$

where k_1 and k_2 are constants, and obtain,

$$B=(2/3)\pi N\left\{\lambda/(kT(n-1))\right\}^{3/(n-1)}\left\{\Gamma\left((n-4)/(n-1)\right)+k_2\right\}$$

$$-(2/3)\pi N\left\{\mu/(kT(m-1))\right\}^{3/(m-1)}k_1 \qquad \ldots \qquad \ldots \quad (15)$$

$$\text{Since } \int_0^{\infty} x^{-t}e^{-bx^{-q}}\,dx=(1/q)(b)^{(1-t)/q}\,\Gamma\left((t-1)/q\right) \qquad \ldots \quad (16)$$

we can write (15) in the form

$$B=(2/3)\pi N\int_0^{\infty}(1/kT)\left(\lambda/r^{(n-3)}\right)e^{-\lambda/[(n-1)(kT)(r^{(n-1)})]}\,dr$$

$$\left[1+k_2/\Gamma\left((n-4)/(n-1)\right)\right]-$$

$$(2/3)\pi N \int_0^\infty (1/kT)\left(\mu/r^{(m-3)}\right)e^{-\mu/[(m-1)(kT)(r^{(m-1)})]}\,dr$$

$$\left[k_1/\Gamma\left((m-4)/(m-1)\right)\right] \quad \ldots \quad \ldots \quad \ldots \quad (17)$$

B is formally expressed by the equation,

$$B=(2/3)\,(\pi N/kT)\int_0^\infty \left(\lambda/r^{(n-3)} - \mu/r^{(m-3)}\right)e^{2jf_1(r)}\,e^{2jf_2(r)}\,dr \ \ldots \quad (18)$$

$$\text{where} \quad 2j=1/kT, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (19)$$

$$\text{and } f_1(r)=-\int_r^\infty \left(\lambda/r^n\right)\,dr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (20)$$

$$=-\ \lambda\Big/(n-1)r^{(n-1)} \quad \ldots \quad \ldots \quad \ldots \quad (21)$$

$$\text{and } f_2(r)=\mu\Big/(m-1)\,r^{(m-1)} \ldots \quad \ldots \quad \ldots \quad \ldots \quad (22)$$

Hence from (17) and (18) we find that the correspondence of (1) and (2) involves

$$\int_0^\infty \left(\lambda/r^{(n-3)} - \mu/r^{(m-3)}\right)e^{2jf_1(r)}\,e^{2jf_2(r)}\,dr$$

$$=\int_0^\infty \lambda/r^{(n-3)}\,e^{2jf_1(r)}\,dr\left[1+k_2/\Gamma\left((n-4)/(n-1)\right)\right]$$

$$-\int_0^\infty \mu/r^{(m-3)}\,e^{-2jf_2(r)}\,dr\left[k_1/\Gamma\left((m-4)/(m-1)\right)\right]\ldots \quad \ldots \quad (23)$$

Comparing (15) with (6), (7), (8), (10) and (11), and using Lennard-Jones' values for λ and μ[1] we should obtain values of k_1 and k_2 which for the same values of (m, n) should be independent of the nature of the gas.

TABLE II.

Gas	Helium	Neon	Hydrogen	Argon	Nitrogen
(m, n)	(5, 9)	(5, 9)	(5, 9)	(5, 9)	(5, 9)
k_1	2·71	3·21	3·16	3·53	3·55
k_2	0·24	0·39	0·42	0·60	0·60
(m, n)	(5, 14⅓)	(5, 14⅓)	(5, 14⅓)	(5, 14⅓)	(5, 14⅓)
k_1	2·98	3·04	2·92	3·65	3·54
k_2	0·23	0·26	0·26	0·61	0·53

Actually as shown in Table II, for (m, n) equal to (5, 9) and (5, 14·3) the values increase from helium to nitrogen. In considering these variations it should be borne in mind that λ and μ for nitrogen, when (m, n) is equal to (5, 14·3), are, respectively, 1535 and 53 times as great as the corresponding values for helium. For (m, n), (5, 9), the corresponding ratios are 121 and 35. The greatest change necessary in any of Lennard-Jones' values of λ and μ to obtain constant values of k_1 and k_2 is about 20 per cent. No conclusions can be drawn as to the way in which k_1 and k_2 vary with (m, n).

These maximum differences of the order of 20 per cent. are less than some of the differences obtained by Lennard-Jones between values calculated from the equation of state and from the viscosity measurements. They involve only changes of 2 per cent. in his "generalised diameters" calculated from the formula

$$\sigma_n = (2/3)\ (\lambda/[(n-1)\ (k)])^{1/(n-1)} \quad \dots \quad \dots \quad \dots \quad (24)$$

[1] It is interesting to note that for the series of gases considered by Lennard-Jones, log λ plotted against log μ gives a straight line; the slope depends on the value of (m, n) taken.

which he uses for the comparison of various values of λ.

On the whole, therefore, the results of the general dimensional method of approach to the virial problem given by the author in the paper cited are not out of harmony with the more rigorous and definite results of Lennard-Jones.

Royal Institute of Science,
Bombay.